

EXPRESS MAIL LABEL NUMBER EL619400465US

Form PTO-1380 REV.10-94)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEYS DOCKET NUMBER RN98116
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/elected office (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (F. KNOWL. SEE 3737 CFR 1.9) 09/763111 NOT APPLICABLE
INTERNATIONAL APPLICATION NO. PCT/FR99/02023	INTERNATIONAL FILING DATE August 20, 1999	PRIORITY DATE CLAIMED August 20, 1998	
TITLE OF INVENTION USE OF TITANIUM DIOXIDE AS ANTI-UV AGENT IN A RUBBER COMPOSITION			
APPLICANT (S) FOR DO/EO/US: Catherine ENJALBERT and Dominique LABARRE			
Applicant herewith submits the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1 <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U S C 371</p> <p>2 <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U S C 371</p> <p>3 <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U S C 371) (f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U S C 371 (b) and PCT Articles 22 and 39(1)</p> <p>4 <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date</p> <p>5 <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U S C 371(c)(2))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p style="margin-left: 20px;">b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US)</p> <p>6 <input checked="" type="checkbox"/> A translation of the International Application into English (35 U S C 371(c)(2)).</p> <p>7 <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210)</p> <p>8 <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U S C 371(c)(2)).</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> have been transmitted by the International Bureau</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> have not been made, however the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 20px;">d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>9 <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U S C 371(c)(3)).</p> <p>10 <input checked="" type="checkbox"/> A oath or declaration of the inventor(s) (35 U S C 371(c)(4)). (signed)</p> <p>11 <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</p> <p>12 <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U S C 371(c)(5)).</p> <p>Items 13 to 18 below concern document(s) or information included:</p> <p>13 <input type="checkbox"/> An information Disclosure Statement under 37 CFR 1 97 and 1 98</p> <p>14 <input checked="" type="checkbox"/> An assignment document for recording A separate cover sheet in compliance with 37 CFR 3 28 and 3 31 is included</p> <p>15 <input checked="" type="checkbox"/> A FIRST preliminary amendment</p> <p>16 <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment</p> <p>17 <input type="checkbox"/> A substitute specification.</p> <p>18 <input type="checkbox"/> A change of power of attorney and/or address letter</p> <p>19 <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail</p> <p>20 <input checked="" type="checkbox"/> Other items or information</p>			
Forms PCT/IB/308 and 332, PCT/ISA/ 210 (English & French Version), PCT/IPEA/ 409, PCT/FR99/02023 as published			

09/763111

US APPLICATION NO. (If known, see 37 CFR 1.51) <div style="font-size: 2em; font-weight: bold; margin-left: 100px;">097/763111</div>	International Application No. PCT/FR99/02023	ATTORNEY DOCKET NUMBER RN98116
		CALCULATIONS PTO ONLY
21 The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1,482) nor International search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$1,000.00 <input checked="" type="checkbox"/> International preliminary examination fee not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$ 860.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1,482) not paid to USPTO but international search (37 CFR 1,445 (a)(2)) fee paid to USPTO..... \$ 710.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1,482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$ 690.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1,482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00 <div style="text-align: center;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div>		<div style="border: 1px solid black; padding: 2px; margin-bottom: 2px;">\$ 860.00</div> <div style="border: 1px solid black; padding: 2px; margin-bottom: 2px;">\$ 0.00</div>
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1,492(e)).		
CLAIMS	NUMBER FILED	NUMBER EXTRA
Total Claims	25-20=	5
Independent Claims	2-3=	0
MULTIPLE DEPENDENT CLAIMS(S) (if applicable) N/A		<input type="checkbox"/>
		RATE
		X\$18.00
		X\$80.00
		<input type="checkbox"/>
TOTAL OF ABOVE CALCULATIONS =		\$ 950.00
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) <input type="checkbox"/>		\$ 0.00
SUBTOTAL =		\$ 950.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1,492 (f)).		\$ 0.00
TOTAL NATIONAL FEE =		\$ 950.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + <input checked="" type="checkbox"/>		\$ 40.00
TOTAL FEES ENCLOSED =		\$ 990.00
		Amount to be refunded \$
		charged \$
a <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed b <input checked="" type="checkbox"/> Please charge my Deposit Account No. 18-1171 in the amount of \$990.00 to cover the above fees. c <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 18-1171 A duplicate copy of this sheet is enclosed.		
NOTE: Where an appropriate time limit under 37 CFR 1,494 or 1,495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.		
SEND ALL CORRESPONDENCE TO: Jean-Louis SEUGNET RHODIA INC. 259 Prospect Plains Road CN 7500 Cranbury, NJ 08512		<div style="text-align: center;"> </div> <div style="text-align: center;"> SIGNATURE <hr style="width: 100%;"/> Jean-Louis SEUGNET NAME Limited Recognition under 37 CFR § 10.9(b) enclosed. </div>
February 16, 2001 DATE		REGISTRATION NUMBER

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: Catherine ENJALBERT and
Dominique LABARRE

National Phase of PCT/FR99/02023

International Filing Date : August 20, 1999

Serial No: N/A

Filing Date: February , 2001

For: USE OF TITANIUM DIOXIDE AS ANTI-UV AGENT IN A RUBBER
COMPOSITION

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

Prior to calculation of filing fee, please enter the following amendment in the
specification and claims:

In the specification:

Page 1, just after the title, please add: - - This application is an application under 35
U.S.C. Section 371 of International Application Number PCT/FR99/02023 filed on
August 20, 1999.- -

In the claims:

Please cancel claims 1 to 24 and add the following new claims 25 to 49:

25. A rubber composition based on at least one elastomer, comprising titanium
dioxide particles as anti-UV agent having an average size of at most 80 nm and at least
partially coated with a layer of at least one metal oxide, hydroxide or oxohydroxide.

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26. The composition as claimed in claims 25, wherein said layer is a layer of at least one silicon or aluminum oxide, hydroxide or oxohydroxide.
27. The composition as claimed in claim 26, wherein said layer is formed from silica, an aluminosilicate or alumina.
28. The composition as claimed in claim 25, wherein said titanium dioxide particles have an average size of between 20 and 70 nm.
29. The composition as claimed in claim 25, wherein the titanium dioxide has a anatase crystal structure.
30. The composition as claimed in claim 25, wherein said titanium dioxide particles have a BET specific surface area of at least 40 m²/g.
31. The composition as claimed in claim 25, wherein said composition comprises at least one elastomer having a glass transition temperature of between -150°C and +20°C.
32. The composition as claimed in claim 25, wherein said composition further comprises at least one reinforcing filler and, optionally, at least one coupling agent or at least one coating agent.
33. The composition as claimed in claim 25, wherein said composition further contains no carbon black.
34. The composition as claimed in claim 25, wherein said composition further comprises at least one organic antioxidant.
35. The composition as claimed in claim 25, wherein said composition has a weight content of titanium dioxide particles of between 0.5 and 8%.

36. A finished article comprising a composition as defined in claim 25
37. A process for protecting a rubber composition against UV radiation, comprising the step of adding to said composition a protecting amount against UV radiation of titanium dioxide particles having an average size of at most 80 nm and at least partially coated with a layer of at least one metal oxide, hydroxide or oxohydroxide.
38. A process as claimed in claim 37, wherein said layer is a layer of at least one silicon or aluminum oxide, hydroxide or oxohydroxide.
39. A process as claimed in claim 38, wherein said layer is formed from silica, an aluminosilicate or alumina.
40. A process as claimed in claim 37, wherein said titanium dioxide particles have an average size of between 20 and 70 nm.
41. A process as claimed in claim 37, wherein the titanium dioxide has a anatase crystal structure.
42. A process as claimed in claim 37, wherein said titanium dioxide particles have a BET specific surface area of at least 40 m²/g.
43. A process as claimed in claim 37, wherein said particles are in powder form.
44. A process as claimed in claim 37, wherein said rubber composition comprises at least one elastomer, having a glass transition temperature of between -150°C and +20°C.

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45. A process as claimed in claim 37, wherein said rubber composition furthermore includes at least one reinforcing filler and, optionally, at least one coupling agent or at least one coating agent.

46. A process as claimed in claim 37, wherein said rubber composition further contains no carbon black.

47. A process as claimed in claim 37, wherein said rubber composition ifurther comprises at least one organic antioxidant.

48. A process as claimed in claim 37, wherein between 0.5 and 8% by mass relative to the total mass of said rubber composition, of titanium dioxide particles is added to said rubber composition.

49. A process as claimed in claim 48, wherein between 1and 5% by mass relative to the total mass of said rubber composition, of titanium dioxide particles is added to said rubber composition.

0075341-0394504

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REMARKS

It is asserted that these amendments do not add new matter. Support for these amendments can be found in the specification and claims as originally filed. Entry of these amendments is respectfully requested.

Respectfully submitted,

By 

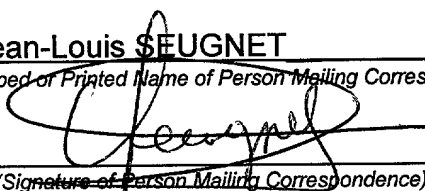
February 16, 2001

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CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10) Applicant(s) : Catherine ENJALBERT and Dominique LABARRE			Docket No. RN98116
Serial No. National Phase of PCT/FR99/02023 Intern. Filing date August 20, 1999	Filing Date February , 2001	Examiner N/A	Group Art Unit N/A
Invention: USE OF TITANIUM DIOXIDE AS ANTI-UV AGENT IN A RUBBER COMPOSITION			
I hereby certify that this Transmittal letter sending documents referred to herein, Specification with Abstract (32 pages) , Declaration/ Power of Attorney (signed), Preliminary Amendment (5 pages), Assignment and Recordation Sheet, Forms PCT/IB/ 308 and 332, PCT/IPEA/409, Forms PCT/ISA/210 (English & French Version), PCT/FR99/02023 as published, Limited Recognition under 37 CFR § 10.9(b).			
<p style="text-align: center;">(Identify type of correspondence)</p> <p>is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231 on February 16, 2001.</p> <p style="text-align: center;">(Date)</p> <p style="text-align: center;">Jean-Louis SEUGNET (Typed or Printed Name of Person Mailing Correspondence)</p> <p style="text-align: center;"> (Signature of Person Mailing Correspondence)</p> <p style="text-align: center;">EL619400465US (“Express Mail” Mailing Label Number)</p> <p style="text-align: center;">Note: Each Paper must have its own certificate of mailing.</p>			

EL619400465US

RN98116USE OF TITANIUM DIOXIDE AS ANTI-UV AGENT IN A RUBBERCOMPOSITION

5 The present invention relates to the use as a
anti-UV agent, in rubber compositions, of particular
titanium dioxide particles.

It also relates to the rubber compositions
thus obtained.

10 Finally, it also relates to the finished
articles based on these compositions, and especially to
tire covers.

Rubber compositions that can be used for the
manufacture of finished articles generally comprise,
15 *inter alia*, one or more elastomers, a reinforcing
filler and a coupling agent (allowing coupling between
the elastomers and the surface of the reinforcing
filler).

It is known to use systems for protecting
20 against UV (ultraviolet radiation) in rubber
compositions for the purpose of limiting the aging of
the latter in light and therefore of preventing their
mechanical properties from degrading.

However, the performance of known UV
25 absorbers, particularly those, such as phenolic
derivatives, employed in "light-colored" rubber
compositions, i.e. those containing no carbon black, is
not always good.

One of the aims of the invention is therefore to propose an anti-UV agent for rubber compositions which is effective, does not migrate to the surface, unlike organic UV absorbers, and can thus preferably
5 retain its protective activity over time.

Another aim of the invention is also to be able to have an anti-UV agent that can be used in rubber compositions containing a reinforcing filler which is not predominantly carbon black, and in
10 particular in "light-colored" rubber compositions, that is to say those containing no carbon black: thus, one of the objectives of the invention is therefore to propose a colorless UV stabilizer which is transparent and therefore does not stain the "light-colored" rubber
15 compositions in which it is incorporated.

To achieve these aims, the subject of the present invention is the use as an anti-UV agent, in a rubber composition, of titanium dioxide particles having an average size of at most 80 nm and at least
20 partially coated with at least one layer of at least one metal oxide, hydroxide or oxohydroxide.

The subject of the invention is also rubber compositions comprising at least one elastomer and at least one such anti-UV agent (or UV absorber).

25 Finally, another subject of the invention consists of the finished articles based on these rubber compositions, especially tire covers.

The invention relates firstly to the use as an anti-UV agent, in a rubber composition, of titanium

dioxide particles having an average size of at most 80 nm and at least partially, preferably completely, coated with at least one layer of at least one metal oxide, hydroxide or oxohydroxide.

5 In general, the composition of this layer is chosen in such a way that it is chemically inert with respect to the elastomers included in the rubber composition to be protected and can react with the coupling agent usually included in this composition.

10 This layer may thus be a layer of at least one silicon and/or aluminum oxide, hydroxide or oxohydroxide.

It may thus be formed from alumina.

15 According to a preferred embodiment, it is formed from silica or from an aluminosilicate.

20 According to another preferred embodiment, it is formed from a layer of silica and of aluminum hydroxide or oxohydroxide, especially with an SiO_2 weight content of approximately 15% and an Al_2O_3 weight content of approximately 5%.

In general, the layer/titanium dioxide weight ratio is between 5 and 100%; usually it is at most 60%; the layer mass is measured by X-ray fluorescence on particles put into suspension.

25 This layer is rather very thin; it usually has a thickness of between 0.5 and 5 nm, in particular between 1 and 3 nm (measured by transmission electron microscopy (TEM)). In addition, it is generally dense.

It should be noted that said titanium dioxide particles may be at least partially coated:

- with a first layer of at least one cerium and/or iron compound; and

5 - with a second layer as described above.

These cerium and/or iron compounds are precursors of cerium or iron oxide, that is to say they are thermally decomposable into cerium or iron oxide. They may be cerium or iron salts. The cerium compounds
10 are preferred.

The titanium dioxide particles employed in the present invention have a number-average size of at most 80 nm, preferably between 20 and 70 nm (measured by transmission electron microscopy (TEM)). This
15 average size is more particularly between 30 and 60 nm, especially between 40 and 50 nm.

Although the titanium dioxide constituting said particles may have a predominantly rutile crystal structure, advantageously it has a predominantly
20 anatase crystal structure, i.e. 50% by weight of said titanium dioxide is of anatase structure. Preferably, 80%, or even almost 100%, by weight of said titanium dioxide is of anatase structure.

In general, said titanium dioxide particles
25 have a BET specific surface area of at least 40 m²/g, in particular at least 70 m²/g, for example at least 100 m²/g; it may be at most 250 m²/g, especially at most 200 m²/g. The BET specific surface area is determined by nitrogen adsorption according to the ASTM D 3663-78

standard drawn up based on the
BRUNAUER - EMMET - TELLER method described in "The
Journal of the American Chemical Society", Vol. 60,
page 309, February 1938.

5 The titanium dioxide particles used in the
present invention usually have a relative density of
between 2.0 and 2.7.

 Preferably, this relative density is between
2.3 and 2.7 when a layer of at least one cerium and/or
10 iron compound is present and is between 2.0 and 2.4
when such a layer is not present.

 Finally, they are preferably used in powder
form.

 The titanium dioxide particles used in the
15 present invention are preferably prepared by
precipitating at least one metal oxide, hydroxide or
oxohydroxide onto the surface of titanium dioxide
particles having an average size of at most 80 nm,
generally having a predominantly anatase crystal
20 structure and usually having a BET specific surface
area of at least 200 m²/g and a relative density of
between 2.3 and 2.7.

 Optionally, at least one cerium and/or iron
compound is precipitated beforehand onto the surface of
25 these starting titanium dioxide particles.

 Such precipitation may be carried out by:

- introducing, into a dispersion of titanium
dioxide particles having the abovementioned
characteristics, precursors of the cerium and/or iron

compounds or metal oxides, hydroxides or oxohydroxides, generally in the form of aqueous salt solutions, and then

- modifying the pH in order to precipitate
5 these compounds or oxides, hydroxides or oxohydroxides onto the titanium dioxide particles.

In general, this precipitation is carried out at a temperature of at least 50°C.

The titanium dioxide particles used according
10 to the invention are not usually calcined, that is to say that they are not usually coated with cerium and/or iron oxides.

The cerium and/or iron compounds are generally cerium or iron salts or hydroxides. In the
15 case of cerium, the compound may be a cerium salt chosen from cerium acetate, cerium sulfate or cerium chloride.

Likewise, when depositing iron, the compound may be an iron chloride, an iron sulfate or an iron
20 acetate.

Cerium acetate and/or iron chloride are most often employed.

In general, the cerium and/or iron compounds are precipitated at a pH of between 4 and 10.

25 It is possible to heat the particle dispersion during this step.

When precipitating silica and an aluminum hydroxide or oxohydroxide, the precipitation may be carried out at acid or basic pH. The pH may be

controlled by adding an acid such as sulfuric acid or by simultaneously and/or alternately introducing an alkaline silicon compound and an acid aluminum compound. In this case, the pH is preferably between 8 and 10.

The silica may be precipitated from a silicon salt such as an alkaline silicate.

The aluminum hydroxide or oxhydroxide may be precipitated from an aluminum salt such as alumina sulfate, sodium aluminate, basic aluminum chloride or aluminum diacetate.

After precipitation, the particles obtained after the treatment may be recovered and washed, one or more times, before being dried or, preferably, being redispersed. This step may be carried out by centrifuging and washing or by ultrafiltration washing. The pH of the washing water is advantageously about 5.5. Next, optionally after one or more further washings of this type, the particles are preferably redispersed, generally in water, and then dried, usually at a temperature of less than 110°C; advantageously, this drying step consists in drying a suspension preferably containing 8 to 30% by weight of said particles by means of an atomizer, for example an APV-type atomizer, with an exit temperature of generally less than 110°C.

The starting titanium dioxide particles have a number-average size of at most 80 nm, preferably between 20 and 70 nm (measured by transmission electron

microscopy (TEM)). This average size is more particularly between 30 and 60 nm, especially between 40 and 50 nm.

Although the titanium dioxide constituting
 5 said starting particles may have predominantly a rutile crystal structure, advantageously it has a predominantly anatase crystal structure, i.e. 50% by weight of said titanium dioxide is of anatase structure. Preferably, 80%, or even almost 100%, by
 10 weight of said titanium dioxide is of anatase structure.

The starting particles usually have a BET specific surface area of at least 200 m²/g, for example at least 250 m²/g.

15 In general, their relative density is between 2.3 and 2.7.

This relative density is especially given by the following formula:

20
$$\text{relative density} = \frac{1}{1 / \rho + V_i}$$

in which:

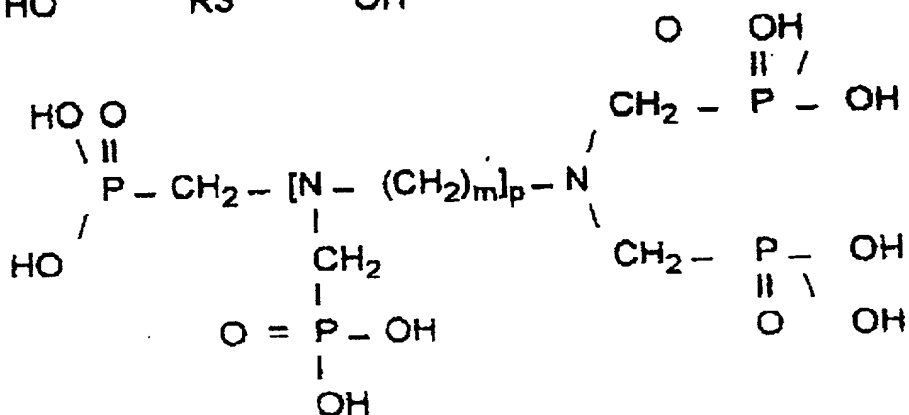
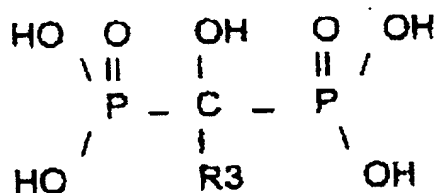
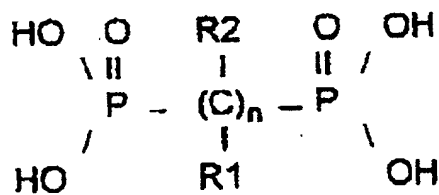
- ρ is the relative density of anatase, i.e. 3.8;
- V_i is the volume provided by the intraparticle pores and is measured by the BJH method. The expression
 25 "volume measured by the BJH method" is understood to mean the volume measured using the BARRETT-JOYNER-HELEND method described in the article entitled "Texture des solides poreux ou divisés

[Texture of porous or divided solids]" in the work *Techniques de l'Ingénieur*, pp. 3645-1 to 3645-13.

To measure the volume provided by the intraparticle pores of the particles according to the invention, when they are in the form of a dispersion, it is essential to follow the measurement protocol consisting in removing the liquid phase of the dispersion and then vacuum-drying the particles at a temperature of 150°C for at least 4 hours.

Such starting particles may be obtained by the hydrolysis of at least one titanium compound A in the presence of at least one compound B chosen from:

(i) organic phosphoric acids of the following formulae:



in which n and m are integers between 1 and 6 and p is an integer between 0 and 5, R1, R2, R3, which are identical or different, representing a hydroxyl, amino, aralkyl, aryl or alkyl group or hydrogen;

5 (ii) acids which have:

- either a carboxyl group and at least two hydroxyl and/or amine groups,
- or at least two carboxyl groups and at least one hydroxyl and/or amine group;

10 (iii) compounds capable of releasing sulfate ions in acid medium;

(iv) salts of the abovementioned acids;

and in the presence of titanium dioxide, usually anatase, seeds advantageously having a size of at most
15 8 nm and in a (TiO₂ present in the seeds)/(titanium present before introducing the seeds into the hydrolysis medium, expressed as TiO₂) weight ratio of preferably between 0.01 and 3%.

The starting solution, intended to be
20 hydrolyzed, is preferably completely aqueous; optionally, another solvent may be added, for example an alcohol, as long as the titanium compound A and the compound B used are then substantially soluble in this mixture.

25 As titanium compound A, a compound chosen from titanium halides, oxyhalides or alkoxides, sulfates, more particularly synthetic sulfates, is in general used.

The expression "synthetic sulfates" is understood to mean titanyl sulfate solutions produced by ion exchange using very pure titanium chloride solutions or by the reaction of sulfuric acid on a
5 titanium alkoxide.

It is preferred to use titanium compounds of the titanium halide or oxyhalide type. The titanium halides or oxyhalides more particularly used in the present invention are titanium fluorides, chlorides,
10 bromides and iodides (or oxyfluorides, oxychlorides, oxybromides and oxyiodides, respectively).

According to a particularly preferred embodiment, the titanium compound is titanium oxychloride TiOCl_2 .

15 The amount of titanium compound A present in the solution to be hydrolyzed is not critical.

The initial solution additionally contains at least one compound B as defined above. Mention may be made, as nonlimiting examples of compounds B, of in
20 particular:

- hydroxypolycarboxylic acids and more particularly hydroxydicarboxylic or hydroxytricarboxylic acids, such as citric acid, maleic acid and tartaric acid;
- 25 - (polyhydroxy)monocarboxylic acids, such as, for example, glucoheptonic acid and gluconic acid;
- poly(hydroxycarboxylic) acids, such as, for example, tartaric acid;

- dicarboxylic monoacids and their corresponding amides, such as, for example, aspartic acid, asparagine and glutamic acid;

- hydroxylated or nonhydroxylated
5 monocarboxylic amino acids, such as, for example, lysine, serine and threonine;

- aminotri(methylenephosphonate), ethylene-
diaminotetra(methylenephosphonate), triethylene-
tetraaminohexa(methylenephosphonate), tetraethylene-
10 pentaaminohepta(methylenephosphonate) or pentaethylene-
hexaaminoocta(methylenephosphonate);

- methylenediphosphonate, 1,1'-ethylenedi-
phosphonate, 1,2-ethylenediphosphonate, 1,1'-propylene-
diphosphonate, 1,3-propylenediphosphonate, 1,6-hexa-
15 methylenediphosphonate, 2,4-dihydroxypentamethylene-
2,4-diphosphonate, 2,5-dihydroxyhexamethylene-2,5-di-
phosphonate, 2,3-dihydroxybutylene-2,3-diphosphonate,
1-hydroxybenzyl-1,1'-diphosphonate, 1-aminoethylene-1-
1'-diphosphonate, hydroxymethylenediphosphonate,
20 1-hydroxyethylene-1,1'-diphosphonate, 1-hydroxy-
propylene-1,1'-diphosphonate, 1-hydroxybutylene-
1,1'-diphosphonate or 1-hydroxyhexamethylene-
1,1'-diphosphonate.

As already indicated, it is also possible to
25 use, as compound B, all the salts of the abovementioned
acids. In particular, these salts are either alkali
metal salts, more particularly sodium salts, or
ammonium salts.

These compounds can also be chosen from sulfuric acid and ammonium or potassium sulfates, and the like.

The compounds B as defined above are generally hydrocarbon-comprising compounds of aliphatic type. In this case, the length of the main hydrocarbon-comprising chain preferably does not exceed 15 carbon atoms, for example, 10 carbon atoms. The preferred compound B is citric acid.

The amount of compound B is not critical. The molar concentration of compound B with respect to that of the titanium compound A is generally between 0.2 and 10% and preferably between 1 and 5%.

Finally, the starting solution comprises titanium dioxide seeds used in a specific way.

Thus, the titanium dioxide seeds used advantageously have a size of less than 8 nm, measured by X-ray diffraction. Use is preferably made of titanium dioxide seeds having a size of between 3 and 5 nm.

Subsequently, the ratio by weight of the titanium dioxide present in the seeds to the titanium present in the hydrolysis medium before introduction of the seeds, that is to say contributed by the titanium compound A, and expressed as TiO_2 is between 0.01 and 3%. This ratio may be between 0.05 and 1.5%. Combining these two conditions with respect to the seeds (size and ratio by weight), together with the process as described above, allows the final size of the titanium

dioxide particles to be precisely controlled, one seed content being associated with one particle size.

Titanium dioxide seeds in the anatase form are generally used, so as to induce precipitation of the titanium dioxide in the anatase form. Usually, due to their small size, these seeds instead exist in the form of poorly crystallized anatase. The seeds are usually in the form of an aqueous suspension composed of titanium dioxide. They can generally be obtained in a known way by a process of neutralizing a titanium salt by a base.

The next step consists in hydrolyzing this starting solution by any means known to a person skilled in the art and generally by heating. In the latter case, the hydrolysis can preferably be carried out at a temperature greater than or equal to 70°C. It is also possible to operate, firstly, at a temperature below the boiling temperature of the medium and, then, to maintain the hydrolysis medium level at the boiling temperature.

Once hydrolysis has been carried out, the titanium dioxide particles obtained are recovered by separation of the precipitated solid from the mother liquors before being redispersed in a liquid medium so as to obtain a titanium dioxide dispersion. This liquid medium can be acidic or basic. It is preferably a basic solution, for example an aqueous sodium hydroxide solution. It is from this dispersion that the step of

precipitating the metal oxides, hydroxides or oxohydroxides, as indicated above, will be carried out.

According to a specific alternative form, after the recovery of the particles obtained following the hydrolysis and before they are redispersed, the particles are neutralized and subjected to at least one washing operation. The particles can be recovered, for example by centrifuging the solution resulting from the hydrolysis; they are subsequently neutralized with a base, for example a sodium hydroxide or aqueous ammonia solution, they are then washed by redispersing them in an aqueous solution, and finally the particles are separated from the aqueous washing phase. After optionally one or more other washing operations of the same type, the particles are redispersed in a liquid or basic solution before the step of precipitating the metal oxides, hydroxides or oxohydroxides.

The mass of titanium dioxide particles used in the invention is usually between 0.5 and 8%, preferably between 1 and 5%, of the total mass of the rubber composition.

The rubber compositions in which said titanium dioxide particles are used as anti-UV agents are, in general, based on one or more elastomers.

More particularly, among suitable elastomers may be mentioned the elastomers having a glass transition temperature of between -150°C and $+20^{\circ}\text{C}$.

As possible elastomers, mention may especially be made of diene elastomers.

For example, mention may be made of natural rubber, polymers or copolymers deriving from aliphatic or aromatic monomers, comprising at least one unsaturated group (such as, especially, ethylene, propylene, butadiene, isoprene and styrene), polybutyl acrylate, or combinations thereof; mention may also be made of silicon elastomers and halogenated elastomers.

The rubber compositions are sulfur vulcanizable.

The invention also relates to the rubber compositions which furthermore include at least one reinforcing filler (for example carbon black, alumina and/or precipitated silica) and, optionally, at least one coupling agent and/or at least one coating agent.

Preferably, the rubber composition includes precipitated, advantageously highly dispersible, silica as reinforcing filler.

In general, this reinforcing filler is formed predominantly, by weight, from precipitated silica, preferably highly dispersible precipitated silica, for example that described in applications EP 0520862, WO 95/09127 and WO 95/09128.

The invention is even more advantageous when the rubber composition is a "light-colored" composition, that is to say it contains no carbon black.

The rubber composition may also include, *inter alia*, an organic antioxidant.

The invention also relates to the finished articles based on the rubber compositions described above. As finished articles, mention may be made of tire covers, particularly the sidewalls and the tread
5 of tires, shoe soles, etc.

The following examples illustrate the invention without however limiting the scope thereof.

EXAMPLE 1

10 Preparation of titanium dioxide particles having an average size of 60 nm, with surface treatment.

1-Hydrolysis

15 The following were added in succession to 394.7 g of a 1.9 mol/kg titanium oxychloride solution:

- 42.02 g of 36% hydrochloric acid;
- 4.73 g of citric acid;
- 574.1 g of purified water;
- 20 - 5.68 g (0.1%/TiO₂) of a suspension containing 1.06% by weight of anatase seeds having a size of between 5 and 6 nm.

The mixture was heated to boiling and kept there for 3 h.

25

2-Recovery of the particles and redispersion

Next, the solution was filtered and the particles obtained were washed with water until the chlorides were completely removed. The particles were

then redispersed at pH 9 (controlled by the addition of sodium hydroxide), the dispersion obtained having a solids content of 20% by weight.

This dispersion was stable. The average size
5 of the particles measured by TEM was 60 nm. X-ray analysis shows that the particles were based on titanium dioxide only in the anatase form.

Their BET specific surface area was $300 \text{ m}^2/\text{g}$.

Their relative density was 2.52
10 ($V_i = 0.14 \text{ cm}^3/\text{g}$).

3-Surface treatment of the particles

750 g of the starting dispersion were introduced into a reactor fitted with a stirrer. Then
15 750 g of purified water were added and the temperature raised to 90°C . The pH of the dispersion was adjusted to 9 by adding sodium hydroxide.

Firstly, a sodium silicate solution (solution containing 335 g/l of SiO_2) containing the equivalent
20 of 22.5 g of SiO_2 and an 80 g/l sulfuric acid solution were continuously and simultaneously introduced in an amount such that the pH was maintained at 9. The rate of introduction of the sodium silicate solution was set at 2 ml/min . Next, a maturing time of 1 hour at 90°C
25 was respected.

Next, an aqueous sodium aluminate solution (240 g/l Al_2O_3 solution) containing the equivalent of 7.5 g of Al_2O_3 was continuously introduced at pH 9 and at 90°C . The rate of introduction of the aluminate

solution was 2 ml/min., the pH being controlled at 9 by simultaneously introducing a 6N aqueous sulfuric acid solution.

When the reactants had been introduced, the dispersion was matured for 2 h at 90°C and then cooled.

The dispersion thus prepared was centrifuged. The cake then obtained was washed three times with water and then redispersed in water. The pH of the dispersion obtained was about 7.7 and the dispersion had a solids content of 10% by weight. The dispersion was then dried by means of an APV-type atomizer, in turbine configuration, the entry temperature being 250°C, the exit temperature being 90°C and the feed rate being about 20 kg/h.

15

4-Characteristics of the particles obtained

The average size of the particles measured by TEM was 60 nm.

Their BET specific surface area was 135 m²/g.

The SiO₂ weight content, measured by X-ray fluorescence, was 14.9% and that of Al₂O₃ was 5%, with respect to the titanium dioxide.

The relative density of the particles prepared was 2.15.

25

EXAMPLE 2

Preparation of titanium dioxide particles having an average size of 45 nm, with surface treatment.

1-Hydrolysis

The following were added in succession to 394.7 g of a 1.9 mol/kg titanium oxychloride solution:

- 5 - 42.02 g of 36% hydrochloric acid;
- 4.73 g of citric acid;
- 574.1 g of purified water;
- 11.36 g (0.2%/TiO₂) of a suspension containing
- 10 1.06% by weight of anatase seeds having a size of
- between 5 and 6 nm.

The mixture was heated to boiling and kept there for 3 h.

2-Recovery of the particles and redispersion

- 15 Next, the solution was filtered and the
- particles obtained were washed with water until the
- chlorides were completely removed. The particles were
- then redispersed at pH 9 (controlled by the addition of
- sodium hydroxide), the dispersion obtained having a
- 20 solids content of 20% by weight.

This dispersion was stable. The average size of the particles measured by TEM was 60 nm. X-ray analysis shows that the particles were based on titanium dioxide only in the anatase form.

- 25 Their BET specific surface area was 300 m²/g.

 Their relative density was 2.52
(V_i = 0.14 cm³/g).

3-Surface treatment of the particles

750 g of the starting dispersion were introduced into a reactor fitted with a stirrer. Then 750 g of purified water were added and the temperature raised to 90°C. The pH of the dispersion was adjusted to 9 by adding sodium hydroxide.

Firstly, a sodium silicate solution (solution containing 335 g/l of SiO_2) containing the equivalent of 22.5 g of SiO_2 and an 80 g/l sulfuric acid solution were continuously and simultaneously introduced in an amount such that the pH was maintained at 9. The rate of introduction of the sodium silicate solution was set at 2 ml/min. Next, a maturing time of 1 hour at 90°C was respected.

Next, an aqueous sodium aluminate solution (240 g/l Al_2O_3 solution) containing the equivalent of 7.5 g of Al_2O_3 was continuously introduced at pH 9 and at 90°C. The rate of introduction of the aluminate solution was 2 ml/min., the pH being controlled at 9 by simultaneously introducing a 6N aqueous sulfuric acid solution.

When the reactants had been introduced, the dispersion was matured for 2 h at 90°C and then cooled.

The dispersion thus prepared was centrifuged. The cake then obtained was washed three times with water and then redispersed in water. The pH of the dispersion obtained was about 7.7 and the dispersion had a solids content of 10% by weight. The dispersion was then dried by means of an APV-type atomizer, in

turbine configuration, the entry temperature being 250°C, the exit temperature being 90°C and the feed rate being about 20 kg/h.

5 4-Characteristics of the particles obtained

The average size of the particles measured by TEM was 45 nm.

Their BET specific surface area was 150 m²/g.

10 The SiO₂ weight content, measured by X-ray fluorescence, was 14.9% and that of Al₂O₃ was 5%, with respect to the titanium dioxide.

The relative density of the particles prepared was 2.15.

15 EXAMPLE 3

The following formulations for industrial rubber were prepared (Table 1: compositions in parts by weight) containing or not containing titanium dioxide particles obtained in Example 1.

20

Table 1

	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5
SBR ⁽¹⁾	100	100	100	100	100
SiO ₂ filler ⁽²⁾	50	50	50	50	50
Si69 silane ⁽³⁾	5	5	5	5	5

TiO ₂ (60 nm) ⁽⁴⁾		1	2		2
antioxid- ant ⁽⁵⁾				2	2

(1) Styrene-butadiene copolymer of the Buna VSL 5525-0 type;

(2) Filler formed by a precipitated silica of Example 12 of EP-A-0520862;

(3) Filler/rubber coupling agent (sold by Dégussa);

(4) UV stabilizer obtained from the above Example 1;

(5) Non-staining phenolic antioxidant called Wingstay L.

10

The compounds were produced using a laboratory Brabender extruder and then pressed at 150°C for 50 minutes in the form of a plaque 2 mm in thickness.

15 The formulations were aged for 89 hours under UV-A (using a UV CON ATLAS apparatus), only one face being exposed. The temperature in the chamber was 57°C.

The determination of the tensile behavior of the unexposed formulations and formulations exposed to the UV-A was carried out at a pull rate of 8 mm/min.

20 Table 2 below gives the tensile strength values (σ_b) and the strain (elongation) at break (ϵ_b), together with the stress values at a strain of 10% ($\sigma_{10\%}$), the change in the stress values at a strain of 10% illustrating the surface hardening of the material.

25

The values under the headings with the suffix (UV) are those of the formulations exposed to UV-A for 89 hours at 57°C.

The values under the headings with the suffix (0) are those of the formulations not exposed to UV-A (or controls), these formulations having, however, also been kept for 89 hours at 57°C, but in the dark.

Table 2

10

	$\epsilon_b(0)$	$\epsilon_b(\text{UV})$	$\sigma_b(0)$	$\sigma_b(\text{UV})$	$\sigma_{10\%}(0)$	$\sigma_{10\%}(\text{UV})$
Compound 1	474	30	2.45	1.79	1.22	2.26
Compound 2	421	148	2.25	2.45	1.21	1.91
Compound 3	440	239	2.24	2.34	1.29	1.75
Compound 4	574	42	2.76	1.96	1.47	2.24
Compound 5	447	307	2.03	2.10	1.25	1.78

ϵ_b expressed in %

σ_b and $\sigma_{10\%}$ expressed in MPa

test piece (specimen) thickness = 1.6 mm.

15

The efficacy as an anti-UV agent of the titanium dioxide particles obtained in Example 1 was determined.

EXAMPLE 4

The following formulations for industrial rubber (Table 3: compositions in parts by weight) containing or not containing titanium dioxide particles obtained in Example 1 (TiO_2 (60 nm)) or in Example 2 (TiO_2 (45 nm)) were prepared.

Table 3

	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5
SBR ⁽¹⁾	100	100	100	100	100
SiO_2 filler ⁽²⁾	50	50	50	50	50
Si69 silane ⁽³⁾	5	5	5	5	5
TiO_2 (60 nm) ⁽⁴⁾		2	4		
TiO_2 (45 nm) ⁽⁵⁾				2	4
antioxid- ant ⁽⁵⁾	2	2	2	2	2

10

- (1) Styrene-butadiene copolymer of the Buna VSL 5525-0 type;
- (2) Filler formed by a precipitated silica of Example 12 of EP-A-0520862;
- 15 (3) Filler/rubber coupling agent (sold by Dégussa);
- (4) anti-UV agent obtained from the above Example 1;

- (5) anti-UV agent obtained from the above Example 2;
- (6) Non-staining phenolic antioxidant called Wingstay L.

5 The compounds were produced using a laboratory Brabender extruder and then pressed at 150°C for 50 minutes in the form of a plaque 2 mm in thickness.

10 The formulations were aged for 89 hours under UV-A (using a UV CON ATLAS apparatus), only one face being exposed. The temperature in the chamber was 57°C.

 The determination of the tensile behavior of the unexposed formulations and formulations exposed to the UV-A was carried out at a pull rate of 8 mm/min.

15 Table 4 below gives the tensile strength values (σ_b) and the strain (elongation) at break (ϵ_b), together with the stress values at a strain of 10% ($\sigma_{10\%}$), the change in the stress values at a strain of 10% illustrating the surface hardening of the material.

20 The values under the headings with the suffix (UV) are those of the formulations exposed to UV-A for 89 hours at 57°C.

 The values under the headings with the suffix (0) are those of the formulations not exposed to UV-A
25 (or controls), these formulations having, however, also been kept for 89 hours at 57°C, but in the dark.

Table 4

	$\varepsilon_b(0)$	$\varepsilon_b(\text{UV})$	$\sigma_b(0)$	$\sigma_b(\text{UV})$	$\sigma_{10\%}(0)$	$\sigma_{10\%}(\text{UV})$
Compound 1	561	35	1.65	2.14	1.30	2.60
Compound 2	445	331	1.81	2.46	1.27	2.00
Compound 3	520	320	1.83	2.12	1.32	1.83
Compound 4	440	305	1.66	1.89	1.19	1.86
Compound 5	507	306	2.07	2.48	1.35	2.01

ε_b expressed in %

σ_b and $\sigma_{10\%}$ expressed in MPa

5 test piece (specimen) thickness = 1.2 mm

It may be seen that the performance obtained for the two products of different average size is quite similar and that the increase in concentration does not
10 produce significantly better results.

However, it should be noted that the transparency of the formulations containing titanium dioxide having an average size of 45 nm is slightly higher than that of the formulations containing
15 titanium dioxide having an average size of 60 nm.

CLAIMS

1. The use as anti-UV agent, in a rubber composition, of titanium dioxide particles having an average size of at most 80 nm and at least partially coated with a layer of at least one metal oxide, hydroxide or oxohydroxide.

2. The use as claimed in claim 1, characterized in that said layer is a layer of at least one silicon and/or aluminum oxide, hydroxide or oxohydroxide.

3. The use as claimed in claim 2, characterized in that said layer is formed from silica, an aluminosilicate or alumina.

4. The use as claimed in one of claims 1 to 3, characterized in that said titanium dioxide particles have an average size of between 20 and 70 nm, in particular between 30 and 60 nm.

5. The use as claimed in one of claims 1 to 4, characterized in that the titanium dioxide has a predominantly anatase crystal structure.

6. The use as claimed in one of claims 1 to 5, characterized in that said titanium dioxide particles have a BET specific surface area of at least 40 m²/g, in particular at least 70 m²/g.

7. The use as claimed in one of claims 1 to 6, characterized in that said particles are used in powder form.

8. The use as claimed in one of claims 1 to 5 7, characterized in that said rubber composition is based on at least one elastomer, said elastomer preferably having a glass transition temperature of between -150°C and $+20^{\circ}\text{C}$.

9. The use as claimed in one of claims 1 to 10 8, characterized in that said rubber composition furthermore includes at least one reinforcing filler and, optionally, at least one coupling agent and/or at least one coating agent.

10. The use as claimed in one of claims 1 to 15 9, characterized in that said rubber composition contains no carbon black.

11. The use as claimed in one of claims 1 to 10, characterized in that said rubber composition includes at least one organic antioxidant.

12. The use as claimed in one of claims 1 to 20 11, characterized in that the mass of titanium dioxide particles used is between 0.5 and 8%, preferably between 1 and 5%, of the total mass of said rubber composition.

13. A rubber composition based on at least 25 one elastomer, containing at least one anti-UV agent, characterized in that said UV stabilizer consists of titanium dioxide particles having an average size of at

most 80 nm and at least partially coated with a layer of at least one metal oxide, hydroxide or oxohydroxide.

14. The composition as claimed in claims 13, characterized in that said layer is a layer of at least one silicon and/or aluminum oxide, hydroxide or oxohydroxide.

15. The composition as claimed in claim 14, characterized in that said layer is formed from silica, an aluminosilicate or alumina.

16. The composition as claimed in one of claims 13 to 15, characterized in that said titanium dioxide particles have an average size of between 20 and 70 nm, in particular between 30 and 60 nm.

17. The composition as claimed in one of claims 13 to 16, characterized in that the titanium dioxide has a predominantly anatase crystal structure.

18. The composition as claimed in one of claims 13 to 17, characterized in that said titanium dioxide particles have a BET specific surface area of at least 40 m²/g, in particular at least 70 m²/g.

19. The composition as claimed in one of claims 13 to 18, characterized in that said composition is based on at least one elastomer having a glass transition temperature of between -150°C and +20°C.

20. The composition as claimed in one of claims 13 to 19, characterized in that said composition includes at least one reinforcing filler and,

optionally, at least one coupling agent and/or at least one coating agent.

21. The composition as claimed in one of claims 13 to 20, characterized in that said composition
5 contains no carbon black.

22. The composition as claimed in one of claims 13 to 21, characterized in that said composition includes at least one organic antioxidant.

23. The composition as claimed in one of
10 claims 13 to 22, characterized in that said composition has a weight content of titanium dioxide particles of between 0.5 and 8%, preferably between 1 and 5%.

24. A finished article based on at least one composition as defined in one of claims 13 to 23.

RN98116

5

**USE OF TITANIUM DIOXIDE AS ANTI-UV AGENT IN A RUBBER
COMPOSITION**

10

Abstract of the Disclosure

The invention concerns the use as anti-UV agent, in an elastomer rubber composition, of titanium dioxide particles of not more than 20 mn in size, said particles being coated with a silica, silico-aluminate or alumina layer. The invention also concerns rubber compositions comprising such an anti-UV agent and finished products based on said composition.

20

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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

USE OF TITANIUM DIOXIDE AS ANTI-UV AGENT IN A RUBBER COMPOSITION

the specification of which (check only one item below):

☐ is attached hereto.

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Serial No. _____

on _____

and was amended

on _____ (if applicable)

☒ was filed as PCT international application

Number **PCT/ FR99/02023**

on **August 20, 1999**

and amended under PCT ARTICLE 19

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I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations. §1.56(a).

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FRANCE	98/10586	20 August, 1998	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
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